

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Shinji YAMAMOTO
Title: EXHAUST GAS PURIFYING
CATALYST
Appl. No.: Unassigned
Filing Date: 05/21/2001
Examiner: Unassigned
Art Unit: Unassigned

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, Applicant respectfully requests that the following amendments be entered into the application:

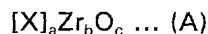
In accordance with 37 CFR §1.121, please substitute for original claims 3-11 the following rewritten versions of the same claims, as amended. The changes are shown explicitly in the attached "Version with Markings to Show Changes Made."

IN THE CLAIMS:

3. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein said catalytic layer contains a H₂ producing catalyst component for functioning to produce hydrocarbons, and a NO_x reducing catalyst component for functioning to reduce nitrogen oxides, said H₂ producing catalyst component being disposed on said HC adsorbing layer and including a HC reforming catalyst component functioning to reform hydrocarbons so as to produce hydrogen and a CO reforming catalyst component functioning to make steam reforming of carbon monoxide, said HC reforming catalyst component containing cerium oxide carrying palladium, said CO reforming catalyst component containing zirconium oxide carrying rhodium.

4. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein said catalytic layer further includes an upstream layer formed at an upstream section of said exhaust gas purifying catalyst, said upstream section being located upstream of said HC reforming catalyst component layer and said CO reforming catalyst component layer relative to flow direction of exhaust gas, said upstream layer containing alumina carrying palladium.

5. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein said zirconium oxide carrying rhodium contains alkaline earth and has a composition represented by the following formula (A):



where X is an alkaline earth metal selected from the group consisting of magnesium, calcium, strontium and barium; a and b are ratios of atoms of elements; and c is a number of oxygen atoms required for satisfying valences of X and Zr, in which a is within a range of from 0.01 to 0.5, b is within a range of from 0.5 to 0.99, and $a + b = 1.0$.

6. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium.

7. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NOx reducing catalyst component containing at least one selected from the group consisting of palladium, platinum, rhodium, alumina, alkali metal and alkaline earth metal.

8. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein said zeolite contains H-type β -zeolite having a Si/2Al ratio ranging from 10 to 500.

9. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein said zeolite contains H-type β -zeolite and at least one of MFI, Y-type zeolite, USY-type zeolite and mordenite.

10. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein said zeolite contains at least one selected from the group consisting of palladium, magnesium, calcium, strontium, barium, silver, yttrium, lanthanum, cerium, neodymium, phosphorus, boron and zirconium.


11. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1, wherein a NO_x reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NO_x reducing catalyst component containing at least one selected from the group consisting of alkali metal and alkaline earth metal, said NO_x reducing catalyst component containing at least one selected from the group consisting of potassium, cesium, magnesium, calcium and barium.

REMARKS

Applicant respectfully requests that the foregoing amendments to Claims 3-11 be entered in order to avoid this application incurring a surcharge for the presence of one or more multiple dependent claims.

Respectfully submitted,

Date May 21, 2001

By 

FOLEY & LARDNER
Washington Harbour
3000 K Street, N.W., Suite 500
Washington, D.C. 20007-5109
Telephone: (202) 672-5414
Facsimile: (202) 672-5399

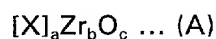
Richard L. Schwaab
Attorney for Applicant
Registration No. 25,479

VERSION WITH MARKINGS TO SHOW CHANGES MADE

3. (Amended) An exhaust gas purifying catalyst as claimed in Claim 1 [or 2], wherein said catalytic layer contains a H₂ producing catalyst component for functioning to produce hydrocarbons, and a NO_x reducing catalyst component for functioning to reduce nitrogen oxides, said H₂ producing catalyst component being disposed on said HC adsorbing layer and including a HC reforming catalyst component functioning to reform hydrocarbons so as to produce hydrogen and a CO reforming catalyst component functioning to make steam reforming of carbon monoxide, said HC reforming catalyst component containing cerium oxide carrying palladium, said CO reforming catalyst component containing zirconium oxide carrying rhodium.

4. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 3] Claim 1, wherein said catalytic layer further includes an upstream layer formed at an upstream section of said exhaust gas purifying catalyst, said upstream section being located upstream of said HC reforming catalyst component layer and said CO reforming catalyst component layer relative to flow direction of exhaust gas, said upstream layer containing alumina carrying palladium.

5. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 4] Claim 1, wherein said zirconium oxide carrying rhodium contains alkaline earth and has a composition represented by the following formula (A):



where X is an alkaline earth metal selected from the group consisting of magnesium, calcium, strontium and barium; a and b are ratios of atoms of elements; and c is a number of oxygen atoms required for satisfying valences of X and Zr, in which a is within a range of from 0.01 to 0.5, b is within a range of from 0.5 to 0.99, and a + b = 1.0.

6. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 5] Claim 1, wherein a NO_x reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium.

7. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 6] Claim 1, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NOx reducing catalyst component containing at least one selected from the group consisting of palladium, platinum, rhodium, alumina, alkali metal and alkaline earth metal.

8. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 7] Claim 1, wherein said zeolite contains H-type β -zeolite having a Si/2Al ratio ranging from 10 to 500.

9. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 8] Claim 1, wherein said zeolite contains H-type β -zeolite and at least one of MFI, Y-type zeolite, USY-type zeolite and mordenite.

10. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 9] Claim 1, wherein said zeolite contains at least one selected from the group consisting of palladium, magnesium, calcium, strontium, barium, silver, yttrium, lanthanum, cerium, neodymium, phosphorus, boron and zirconium.

11. (Amended) An exhaust gas purifying catalyst as claimed in [any of Claims 1 to 10] Claim 1, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NOx reducing catalyst component containing at least one selected from the group consisting of alkali metal and alkaline earth metal, said NOx reducing catalyst component containing at least one selected from the group consisting of potassium, cesium, magnesium, calcium and barium.

6/PRTS

DESCRIPTIONEXHAUST GAS PURIFYING CATALYST5 FIELD OF THE INVENTION

This invention relates to improvements in an exhaust gas purifying catalyst, and more particularly to improvements in an exhaust gas purifying catalyst for effectively reducing nitrogen oxides in an oxygen-excessive exhaust gas

10 BACKGROUND TECHNIQUE

Hitherto catalysts for simultaneously oxidizing carbon monoxide (CO) and hydrocarbons (HC) and reducing nitrogen oxides (NOx) have been extensively used as exhaust gas purifying catalysts installed to internal combustion engines of automotive vehicles and
15 the like. A typical example of these catalysts is disclosed in Japanese Patent Publication No. 58-20307, in which an alumina coat layer is formed on a refractory substrate and contains noble metals such as Pd, Pt and/or Rh and additionally contains, as assistant catalyst, oxides of rare earth metal such as Ce and/or La and/or of base metal
20 such as Ni, if necessary.

However, such a catalyst is largely affected by an exhaust gas temperature and a set air-fuel ratio of the engine, and therefore cannot reduce NOx particularly when exhaust gas of the engine is oxygen-excessive (i.e., has an air-fuel ratio leaner than
25 stoichiometric value). In this regard, Japanese Patent No. 2600429 discloses a so-called rich spike process as a method of reducing NOx when exhaust gas of the engine is oxygen-excessive, using a NOx reducing catalyst for promoting reduction reaction of NOx. In this method, NOx is trapped when exhaust gas takes an
30 oxygen-excessive or lean atmosphere (having the air-fuel ration leaner than the stoichiometric value), and then the trapped NOx is released and reduced by temporarily lowering an oxygen concentration of exhaust gas so that exhaust gas takes exhaust gas

takes a rich atmosphere (having the air-fuel ratio richer than the stoichiometric value).

DISCLOSURE OF THE INVENTION

Drawbacks have been encountered in the above NOx
5 reducing method using the rich spike process, as set forth below. That is, the NOx reducing method requires to periodically lowering the oxygen concentration in exhaust gas in an engine operating region in which exhaust gas takes the oxygen-excessive atmosphere. Additionally, in order to make reduction reaction of NOx under a
10 condition where the oxygen concentration has been lowered, it is required to supply a large amount of HC and CO as reducing agents. This makes it impossible to obtain fuel economy improvement effect due to vehicle running on oxygen-excessive air-fuel mixture having an air-fuel ratio leaner than the stoichiometric value.

15 Additionally, in the above NOx reducing method, the catalyst contains a large amount of alkali metal and alkaline earth metal for the purpose of trapping NOx in the oxygen-excessive atmosphere of exhaust gas, and therefore a catalytic activity (for oxidation) of platinum and rhodium cannot be sufficiently exhibited when
20 exhaust gas is low in temperature. Furthermore, in order to sufficiently oxidize or remove HC and CO components which have not been consumed under NOx reduction reaction, it is required to oxidize or remove the components by making oxidation reaction on the NOx reducing catalyst, or otherwise by a three-way catalyst disposed downstream of the NOx reducing catalyst for reducing NOx.
25

However, such the NOx reducing catalyst or the three-way catalyst disposed downstream of the NOx reducing catalyst are located considerably far from the engine, and therefore the temperature of exhaust gas flown to the catalysts are unavoidably
30 lowered, thereby making it impossible to exhibit a sufficient oxidizing performance for HC and CO. Particularly immediately after engine starting, sufficient oxidation of HC and CO is difficult to be made. Additionally, when HC and CO components in exhaust gas

are increased to lower an oxygen concentration in exhaust gas and to reduce NOx as discussed above, it is impossible to make vehicle running under lean-burn operation, thereby exhibiting an insufficient fuel economy improvement effect.

5 It is, therefore, an object of the present invention is to provide an improved exhaust gas purifying catalyst which can effectively overcome drawbacks encountered in conventional techniques for reducing NOx in exhaust gas.

10 Another object of the present invention is to provide an improved exhaust gas purifying catalyst which can effectively remove NOx, HC and CO from exhaust gas while obtaining a high fuel economy improvement effect.

15 A further object of the present invention is to provide an improved exhaust gas purifying catalyst for an internal combustion engine, which can remove NOx in exhaust gas at a high efficiency by using hydrogen (H₂) as reducing agent and effectively remove HC and CO particularly during a low temperature engine operation immediately after engine starting, while obtaining a high fuel economy improvement effect upon making lean-burn operation of
20 the engine.

25 An aspect of the present invention resides in an exhaust gas purifying catalyst comprising a monolithic substrate. A HC adsorbing layer for adsorbing hydrocarbons (HC) is formed on the monolithic substrate. A catalytic layer for producing hydrogen (H₂) and reducing NOx is formed on the HC adsorbing layer. The catalytic layer functions to produce hydrogen (H₂) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NOx) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.

30 Another aspect of the present invention resides in an exhaust gas purifying system for an internal combustion engine. The exhaust gas purifying system comprises an exhaust gas purifying catalyst including a monolithic substrate. A HC adsorbing layer for

adsorbing hydrocarbons (HC) is formed on the monolithic substrate. A catalytic layer for producing hydrogen (H₂) and reducing NO_x is formed on the HC adsorbing layer. The catalytic layer functions to produce hydrogen (H₂) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO_x) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas. A device is provided to control combustion in the engine to produce exhaust gas, to be brought into contact with the catalytic layer, having a composition meeting a relation [(a concentration of hydrogen / a concentration of total reducing components) ≥ 0.3].

A further aspect of the present invention resides in a method of producing an exhaust gas purifying catalyst. The method comprises (a) preparing a monolithic substrate; (b) forming a HC adsorbing layer on the monolithic layer, to adsorb hydrocarbons (HC); and (c) forming a catalytic layer on the HC adsorbing layer, to produce hydrogen (H₂) and reduce NO_x, the catalytic layer functioning to produce hydrogen (H₂) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO_x) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a fragmentary transverse sectional view of an example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, and functions of respective layers in the structure;

Fig. 2 is a fragmentary longitudinal sectional view of another example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, and functions of respective layers in the structure;

Fig. 3 is a fragmentary longitudinal sectional view of a further example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, in connection of Examples;

5 Fig. 4 is a fragmentary longitudinal sectional view of a still further example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, in connection of Examples;

10 Fig. 5 is a fragmentary longitudinal sectional view of a still further example of an exhaust gas purifying catalyst according to the present invention, showing a coat layer structure defining a cell through which exhaust gas flows, in connection of Examples; and

15 Fig. 6 is a schematic illustration of an exhaust gas purifying system (including the exhaust gas purifying catalyst according to the present invention) incorporated with an automotive internal combustion engine, the engine being used as an evaluation engine system for evaluating emission performance of the exhaust gas purifying catalysts according to the present invention.

THE BEST MODE FOR CARRYING OUT THE INVENTION

20 According to the present invention, an exhaust gas purifying catalyst comprises a monolithic substrate. A HC adsorbing layer for adsorbing hydrocarbons (HC) is formed on the monolithic substrate. A catalytic layer for producing hydrogen (H_2) and reducing NOx is formed on the HC adsorbing layer. The catalytic
25 layer functions to produce hydrogen (H_2) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NOx) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.

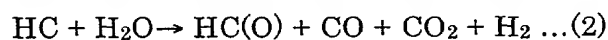
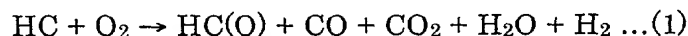
30 The HC adsorbing layer preferably contains zeolite (HC adsorbing material) capable of adsorbing hydrocarbons, as a main component. In case that the exhaust gas purifying catalyst is for an internal combustion engine, for example, of an automotive vehicle, the HC adsorbing layer can adsorb HC during a cold operation of the

engine, i.e., when the catalyst has been still at a low temperature immediately after engine starting, and release HC during a warm-up operation of the engine, i.e., when the catalyst is at a temperature within a range of from 100 to 300 °C. It will be understood that cold stage and warm-up stages of the catalyst are respectively during the cold operation and the warm-up operation of the engine.

The catalytic layer for producing H₂ and reducing NO_x functions to produce hydrogen (H₂) from hydrocarbons released from the HC adsorbing layer under reforming reactions of HC and CO as discussed below. Additionally, the catalytic layer functions also to produce hydrogen (H₂) from hydrocarbons and/or carbon monoxide in exhaust gas discharged from the engine during a steady state engine operation. Hydrogen (H₂) thus produced can effectively react with NO_x, serving as reducing agent.

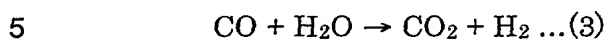
It is to noted that reactivity of hydrogen with NO_x is high, and therefore it is assumed that NO_x emitted from the engine can be effectively reduced even during the warm-up stage of from a time immediately after the engine starting to a time making lean-burn operation of the engine although the NO_x reducing catalyst component contained in the catalytic layer has not been sufficiently raised in temperature and sufficiently activated. In the lean-burn operation, the engine is supplied mainly with air-fuel mixture having an air-fuel ratio leaner than a stoichiometric value, thereby discharging exhaust gas (or oxygen-excessive atmosphere) having an air-fuel ratio leaner than a stoichiometric value.

The above HC and CO reforming reactions carried out in the catalytic layer is divided in general into reforming reaction of HC and steam reforming reaction of CO. The HC reforming reaction is assumed to be represented by the following reaction formulae (1) and (2):



where HC(O) indicates HC produced under the reforming reaction of HC.

The CO steam reforming reaction is assumed to be represented by the following reaction formula (3):



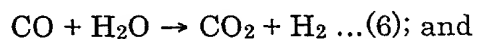
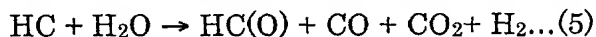
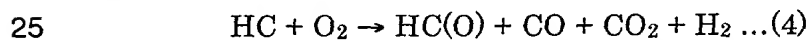
The catalytic layer contains a H₂ producing catalyst component for functioning to produce hydrocarbons, and a NO_x reducing catalyst component for functioning to reduce nitrogen oxides. The H₂ producing catalyst component is disposed on the HC adsorbing layer and including a HC reforming catalyst component functioning to reform hydrocarbons so as to produce hydrogen, and a CO reforming catalyst component functioning to make steam reforming of carbon monoxide. The HC reforming catalyst component preferably contains cerium oxide carrying palladium.
10 The CO reforming catalyst component preferably contains zirconium oxide carrying rhodium.

Preferably, the HC reforming catalyst component forms a first layer disposed on the monolithic substrate, and the CO reforming catalyst forms a second layer, in which the second layer is formed on the first layer, so that the catalytic layer takes a multiple layer structure. Otherwise, the HC reforming catalyst component and the CO reforming catalyst are mixed to form a single layer disposed on the monolithic substrate on the HC adsorbing layer, so that the catalytic layer takes a single layer structure. Otherwise, the
20 HC reforming catalyst component forms a first layer disposed on the monolithic substrate, and the CO reforming catalyst component forms a second layer, in which the second layer is formed downstream of the first layer relative to flow direction of exhaust gas.

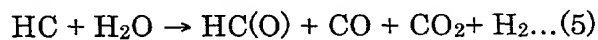
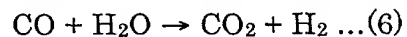
30 As shown in Fig. 1, HC adsorbed in the HC adsorbing layer immediately after engine starting and released from the HC adsorbing layer at the warm-up stage of the catalyst is first subjected to partial oxidation in the HC reforming layer so that HC

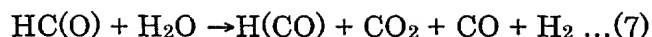
is converted into partial oxide (HC(O) corresponding to partially oxidized HC), CO and H₂. Then, the partial oxide, CO and H₂ are converted into H₂ in the CO reforming layer. As a result, even at the catalyst warm-up stage, H₂ is produced under reforming of HC and CO, and therefore NO_x can be reduced. Additionally, during an engine operating range accomplishing the lean-burn operation, H₂ is supplied in the catalytic layer, thereby reducing NO_x after completion of the catalyst warm-up. It will be understood that the HC reforming layer and the CO reforming layer may be arranged side by side (or located respectively on the upstream and downstream sides) in a direction of flow of exhaust gas since it is sufficient that HC released from the HC adsorbing layer undergoes first the HC reforming reactions, and subsequently the CO steam reforming reaction.

Additionally, in order to produce H₂ under reforming of HC, it is preferable that the above-discussed HC reforming layer contains cerium oxide carrying Pd. In order to produce H₂ under steam reforming of CO, it is preferable that the above-discussed CO reforming layer contains zirconium oxide carrying Rd. By virtue of these noble metals and oxides contained, reactions represented by the following formulae (4), (5) and (6) are assumed to be mainly carried out in the HC reforming layer when exhaust gas is introduced or passed into the exhaust gas purifying catalyst of the present invention:



Additionally, reactions represented by the following formulae (5), (6) and (7) are assumed to be mainly carried out in the CO reforming layer when exhaust gas is introduced or passed into the exhaust gas purifying catalyst of the present invention:





As a result of the above reactions, H_2 is produced while exhaust gas components, particularly HC and CO are oxidized to be removed.

5 Further, the catalytic layer for producing H_2 and reducing NOx contains not only the catalyst components for producing H_2 but also the catalyst components for reducing NOx. Thus, even with such a single catalyst, H_2 serving as the reducing agent for NOx can be produced while effectively reducing NOx.

10 Furthermore, in order to further promote production of H_2 from HC and CO in exhaust gas even after the engine warm-up stage, it is preferable that an upstream section of the catalytic layer for producing H_2 and reducing NOx is replaced with a catalytic (upstream) layer containing alumina carrying Pd. The upstream
15 section is located at an upstream side with respect to flow of exhaust gas discharged from the engine. More specifically, such a preferable mode is as follows: A HC partial oxidation or reforming layer containing alumina carrying Pd is formed on the upstream side or section of the HC adsorbing layer while the HC reforming layer
20 containing cerium oxide carrying Pd and the CO reforming layer containing zirconium oxide carrying Pd are formed on a downstream side or section of the HC adsorbing layer.

An example of this preferable mode is shown in Fig. 2; however, the exhaust gas purifying catalyst of the present invention
25 is not limited to this example. In the example of Fig. 2, the CO reforming layer is formed on the HC reforming layer on the downstream side or section of the HC adsorbing layer. Additionally, the HC partial oxidation layer on the upstream side or section of the HC adsorbing layer is in contact with the HC reforming layer and
30 the CO reforming layer on the downstream side or section of the HC adsorbing layer. In the exhaust gas purifying catalyst as shown in Fig. 2, after the warm-up stage of the catalyst, it is assumed that the HC partial oxidation layer (containing alumina carrying Pd) on the

upstream side or section converts HC contained in exhaust gas into HC(O) and CO under partial oxidation; then the HC reforming layer promotes production of H₂ under the reforming reaction of H(CO); and subsequently the CO reforming layer produces H₂ under steam reforming reaction of CO. Accordingly, according to this example, H₂ can be supplied even after completion of warm-up of the catalyst, subsequent to the warm-up stage of the catalyst. This makes it possible to reduce and remove NO_x in exhaust gas having the lean air-fuel ratio or in the oxygen-excess atmosphere.

As discussed above, in operation of the exhaust gas purifying catalyst of the present invention, H₂ is used as the reducing agent, in place of HC and CO which have been conventionally used as reducing agent. In this connection, it is preferable that composition of exhaust gas to be brought into contact with the NO_x reducing catalyst component meets a relation [(a concentration of hydrogen / a concentration of total reducing components) \geq 0.3]. Such exhaust gas composition meeting the above relation can be realized, for example, by controlling combustion to be made in combustion chambers of an internal combustion engine, i.e., by controlling fuel injection amount (amount of fuel injected from a fuel injector), fuel injection timing (timing at which fuel is injected from the fuel injector), spark timing (timing at which a spark plug generates spark), opening and/or closing timings of intake and/or exhaust valves.

For example, as shown in Fig. 6, the above relation in exhaust gas was accomplished by controlling the fuel injection amount and fuel injection timing of fuel to be injected from a fuel injection system 11 by control signals fed from an electronic control unit (ECU) 13. The electronic control unit 13 is arranged to be supplied with signals representative of intake air amount (amount of air to be sucked into the engine), combustion pressure (pressure within combustion chamber under combustion) and exhaust gas temperature (temperature of exhaust gas discharged from the

are ratios of atoms of elements; and c is a number of oxygen atoms required for satisfying valences of X and Zr, in which a is within a range of from 0.01 to 0.5, b is within a range of from 0.5 to 0.99, and $a+b = 1.0$.

5 It is to be noted that the alkaline earth metal contained in the zirconium oxide makes it possible to obtain a high catalytic activity throughout a long time use (including the initial time in use).

10 Additionally, it is preferable that the NOx reducing catalyst component for reducing NOx is contained in at least one of the HC adsorbing layer, the catalytic layer for producing H₂ and reducing NOx and the upstream side catalytic layer containing alumina carrying Pd. Accordingly, Pt and/or Rh serving as the NOx reducing catalyst components may be contained in all of the HC
15 adsorbing layer, the HC reforming layer, the CO reforming layer of the catalytic layer for producing H₂ and reducing NOx, and the upstream-side catalytic layer containing alumina carrying Pd. By virtue of the NOx reducing catalyst component, H₂ can be produced in the warm-up stage of the catalyst while NOx emitted in the
20 catalyst warm-up stage can be effectively reduced and removed. Additionally, NOx emitted can be also effectively reduced and removed during engine operational control under supply of air-fuel mixture having lean air-fuel ratio to the engine (i.e., the oxygen-excess atmosphere).

25 In addition to the fact that the NOx reducing catalyst component is contained in at least one of the respective catalytic layers, it is also preferable that a further catalytic layer for reducing NOx may be formed on the catalytic layer for producing H₂ and reducing NOx. Otherwise, the further catalytic layer may be formed
30 on the catalytic layer for producing H₂ and reducing NOx without the NOx reducing catalyst component being contained in at least one of the respective catalytic layers. Otherwise, the exhaust gas purifying catalyst of the present invention may be disposed

upstream of a NOx reducing catalyst in the exhaust gas passageway through which exhaust gas discharged from the engine flows.

Furthermore, the NOx reducing catalyst component including Pd, alumina, alkali metal(s) and/or alkaline earth metal(s) may be contained in at least one of the HC adsorption layer, the HC partial oxidation layer, the CO reforming layer and/or the upstream section of the catalytic layer. By virtue of the above NOx reducing catalyst component contained in the exhaust purifying catalyst, NOx emitted from the engine can be effectively reduced and removed throughout whole engine operating regions from a time immediately after engine starting to a time accomplishing a steady state engine operation providing the oxygen-excess atmosphere.

It is preferable that the content of the above alkali metal(s) and/or alkaline earth metal(s) in the whole catalytic layer (formed on the HC adsorbing layer) is not less than 80 % by weight of a total content of alkali metal(s) and alkaline earth metal(s) contained in the exhaust gas purifying catalyst. With such a content, NOx emitted from the engine can be effectively trapped by the alkali metal(s) and/or alkaline earth metal(s) in a lean region (in which exhaust gas has air-fuel ratio leaner than stoichiometric level). If the content is less than 80 % by weight, a sufficient NOx trapping performance cannot be obtained.

In order to realize the above content (of 80 % by weight) of alkali metal(s) and/or alkaline earth metal(s), it is preferable that the alkali metal(s) and/or alkaline earth metal(s) are used as water-insoluble compound(s) and/or slightly water-soluble compound(s).

Zeolite used in the above HC adsorbing layer is selected from known zeolites; however, it is preferable to select zeolite(s) which can exhibit a sufficient HC adsorbing performance particularly in a temperature region of from ordinary temperature to a relatively high temperature and even in an atmosphere in presence of water, and a high durability. A preferable example of

such zeolites is H-type β -zeolite having a Si/2Al ratio ranging from 10 to 500; however, zeolite to be used in the HC adsorbing layer is not limited to this. If zeolite has a Si/2Al ratio smaller than 10, it cannot effectively adsorb HC because impeding HC adsorption by
5 water coexisting in exhaust gas is considerable. If zeolite has a Si/2Al ratio larger than 500, HC adsorbing performance of zeolite may be lowered.

Furthermore, it is also preferable to select at least one of MFI, Y-type zeolite, USY-type zeolite and/or mordenite which are
10 different from each other in diameter and structure of fine pores formed in the zeolite, and to mix the selected one(s) with the above-mentioned H-type β -zeolite so as to prepare the zeolite to be contained in the HC adsorbing layer. Such selection is made taking account of the components of exhaust gas discharged from the engine,
15 resulting in effective adsorption of HC in the HC adsorbing layer.

It will be understood that the above H-type β -zeolite has a sufficient HC adsorption performance; however, the H-type β -zeolite may carry Pd, Mg, Ca, Sr, Ba, Ag, Y, La, Ce, Nd, P, B and/or Zr by using conventional methods such as an ion exchange method, an
20 impregnation method or a dipping method, thereby further improving HC adsorption performance and HC release-suppression performance of the zeolite.

An example of the monolithic substrate used in the exhaust gas purifying catalyst is a honeycomb-type monolithic
25 substrate. The honeycomb-type monolithic substrate is formed of ceramic materials such as cordierite ceramic, or may be formed of metal such as ferrite stainless steel. Otherwise, powder serving as the catalyst components may be formed into a honeycomb shape. The honeycomb-type monolithic substrate is formed with a plurality of
30 cells which axially extend. Each cell is defined by walls which axially extend and have a thickness

EXAMPLES

0535369-052404

The present invention will be more readily understood with reference to the following Examples in comparison with Comparative Example; however, these Examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

[Preparation of Catalytic Powder of HC Reforming Layer]

Cerium oxide (CeO_2) powder was impregnated with an aqueous solution of palladium (Pd) nitrate, followed by drying and firing, thereby preparing Pd-carried cerium oxide powder A whose concentration of Pd was 10 % by weight.

Subsequently, powder B was prepared by repeating the same operation as that for Powder A with the exception that $\text{Zr}_{0.1}\text{Ce}_{0.9}\text{O}_2$ was used in place of CeO_2 .

Powder C was prepared by repeating the same operation as that for Powder A with the exception that $\text{Zr}_{0.2}\text{Ce}_{0.8}\text{O}_2$ was used in place of CeO_2 .

Powder D was prepared by repeating the same operation as that for Powder A with the exception that $\text{Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$ was used in place of CeO_2 .

Powder E was prepared by repeating the same operation as that for Powder A with the exception that $\text{Zr}_{0.9}\text{Ce}_{0.1}\text{O}_2$ was used in place of CeO_2 .

Powder F was prepared by repeating the same operation as that for Powder A with the exception that Powder F had a Pd concentration of 5 % by weight.

[Preparation of Catalytic Powder for CO Reforming Layer]

Powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$ was impregnated with an aqueous solution of rhodium (Rh) nitrate, followed by drying and firing, thereby preparing Rh-carried zirconium oxide powder G whose Rh concentration was 6 % by weight.

Subsequently, Powder H was prepared by repeating the same operation as that for Powder G with the exception that powder of $\text{Mg}_{0.1}\text{Zr}_{0.9}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

Powder I was prepared by repeating the same operation as that for Powder G with the exception that powder of $\text{Ba}_{0.1}\text{Zr}_{0.9}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

5 Powder J was prepared by repeating the same operation as that for Powder G with the exception that powder of $\text{Sr}_{0.2}\text{Zr}_{0.8}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

Powder K was prepared by repeating the same operation as that for Powder G with the exception that powder $\text{Ca}_{0.1}\text{Mg}_{0.1}\text{Zr}_{0.8}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

10 Powder L was prepared by repeating the same operation as that for Powder G with the exception that powder $\text{Ca}_{0.1}\text{Ba}_{0.05}\text{Mg}_{0.05}\text{Zr}_{0.8}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

Powder M was prepared by repeating the same operation as that for Powder G with the exception that powder $\text{Ca}_{0.01}\text{Zr}_{0.99}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

Powder N was prepared by repeating the same operation as that for Powder G with the exception that powder $\text{Ca}_{0.55}\text{Zr}_{0.45}\text{O}_2$ was used in place of the powder of $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$.

[Preparation of Catalytic Powder of HC oxidizing layer]

20 Powder of activated alumina (Al_2O_3) was impregnated with an aqueous solution of palladium (Pd) nitrate, followed by drying and firing, thereby preparing Pd-carried alumina powder O whose Pd concentration was 15 % by weight.

25 Subsequently, powder P was prepared by repeating the same operation as that for powder O with the exception that powder of powder of activated alumina (Al_2O_3) containing 3 % by weight of Ce was used in place of the powder of Al_2O_3 .

30 Powder Q was prepared by repeating the same operation as that for powder O with the exception that powder of activated alumina (Al_2O_3) containing 3 % by weight of Zr was used in place of the powder of Al_2O_3 .

Powder R was prepared by repeating the same operation as that for powder O with the exception that powder of alumina

(Al₂O₃) containing 3 % by weight of La was used in place of the powder of Al₂O₃.

Powder S was prepared by repeating the same operation as that for powder O with the exception that powder of alumina (Al₂O₃) containing 10 % by weight of Zr was used in place of the powder of Al₂O₃.

[Preparation of Catalytic Powder of NO_x reducing layer]

Powder of activated alumina (Al₂O₃) was impregnated with an aqueous solution of palladium (Pd) nitrate, followed by drying and firing, thereby preparing Pd-carried alumina powder T whose Pd concentration was 8 % by weight.

Powder of activated alumina (Al₂O₃) was impregnated with an aqueous solution of dinitrodiammine platinum, followed by drying and firing, thereby preparing Pt-carried alumina powder U whose Pt concentration was 6 % by weight.

Powder of activated alumina (Al₂O₃) was impregnated with an aqueous solution of rhodium (Rh) nitrate, followed by drying and firing, thereby preparing Rh-carried alumina powder V whose Rh concentration was 4 % by weight.

EXAMPLE 1

[Preparation of Catalyst]

β-Zeolite (Si/2Al = 25) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z1 having 100 g of a zeolite coat per one liter of the monolithic substrate.

Subsequently, 706 g of the powder A, 14g of nitric acid-acidic alumina binder and 800 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the

0956369-052401

catalyst Z1, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst A provided with a coat formed on the catalyst Z1 and having a weight of 72 g per one liter of the monolithic substrate. The catalyst A carried 7.06 g of Pd per one liter of the monolithic substrate.

10 Additionally, 588 g of the powder G, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst A, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst AG1 (shown in Table 2) provided with a coat in an amount of 60 g per one liter of the monolithic substrate. The catalyst AG1 carried 3.53 g per one liter of the monolithic substrate. The catalyst AG1 took a three-layer structure as shown in Fig. 3.

20 In the column of "HC adsorbing layer" in Table 2, " β (Si/2Al=25)" indicates the fact that the HC adsorbing layer contained β -zeolite (having a Si/2Al ratio of 25). In the column of "First layer" in Table 2, "A" indicates the fact that the First layer contained the powder A. In the column of "Second layer" in Table 2, "G" indicates the fact that the Second layer contained the powder G.

The HC adsorbing layer, the First layer, the Second layer and the Third layer shown in Table 2 are correspondingly illustrated in Fig. 3.

25 [Preparation of NO_x reducing Catalyst]

30 The powder T in an amount of 618 g, 530 g of the powder U, 88 g of the powder V, 20 g of sodium hydroxide (calculated as Na₂O), 20 g of barium acetate (calculated as BaO), 14 g of nitric acid-acidic alumina binder and 1500 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 400 cells per square inch and having a thickness of walls (defining each cell) of 6 mil, so that the walls of the

cells were coated with the slurry. The thus coated monolithic substrate was dried and fired thereby to obtain a catalyst N1 provided with a coat formed on the monolithic substrate and having a weight of 147 g per one liter of the monolithic substrate. The catalyst N1 carried 4.94 g of Pd, 3.18 g of Pt and 0.35 g of Rh per one liter of the monolithic substrate. The catalyst N1 took such a structure that a single layer of coat was formed on the monolithic substrate.

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying system of Example 1 was constructed by disposing the catalyst AG1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO_x reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst AG1 and located at the position of the catalyst 2.

EXAMPLES 2 to 7

[Preparation of Catalyst]

Catalysts AG2, AG4, AG5, AG6 and AG7 (shown in Table 2) corresponding respectively to Examples 2, 3, 4, 5, 6 and 7 were obtained repeating the above preparation operation for the catalyst AG1 with the exception that β -zeolite ($\text{Si}/2\text{Al} = 25$) was replaced with other HC adsorbing materials shown in Table 2, respectively.

In the column of "HC adsorbing layer" in Table 2, " $\beta(\text{Si}/2\text{Al} = 15)$ " indicates the fact that the HC adsorbing layer contained β -zeolite (having a $\text{Si}/2\text{Al}$ ratio of 15); " $\beta(\text{Si}/2\text{Al} = 300)$ " indicates the fact that the HC adsorbing layer contained β -zeolite (having a $\text{Si}/2\text{Al}$ ratio of 300); " $\beta(\text{Si}/2\text{Al} = 25) + \text{MFI} (= 30)$ " indicates the fact that the HC adsorbing layer contained a mixture of β -zeolite (having a $\text{Si}/2\text{Al}$ ratio of 25) and MFI (having a $\text{Si}/2\text{Al}$ ratio of 30); " $\beta(=25) + \text{USY}(=15)$ " indicates the fact that the HC adsorbing layer contained a mixture of β -zeolite (having a $\text{Si}/2\text{Al}$ ratio of 25) and USY-type zeolite having a $\text{Si}/2\text{Al}$ ratio of 15); " $\text{Ag,P-}\beta(=25)$ " indicates the fact that the HC

adsorbing layer contained β -zeolite (having a Si/2Al ratio of 25) containing and P; and "Pd- β (=25)" indicates the fact that the HC adsorbing layer contained β -zeolite (having a Si/2Al ratio of 25) containing.

5 [Construction of Exhaust Gas Purifying System]

Each of exhaust gas purifying systems of Examples 2, 3, 4, 5, 6 and 7 was constructed by disposing the catalyst AG2, AG3, AG4, AG5, AG6 or AG7 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO_x reducing catalyst) N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst AG2, AG3, AG4, AG5, AG6 or AG7 and located at the position of the catalyst 2.

EXAMPLE 8

15 [[Preparation of Catalyst]

β -Zeolite (Si/2Al = 25) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z1 having 100 g of a zeolite coat per one liter of the monolithic substrate.

Subsequently, 706 g of the powder B, 14g of nitric acid-acidic alumina binder and 800 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst Z1, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst B provided with a coat formed on the catalyst Z1 and having a weight of 72 g per one liter of the monolithic substrate. The catalyst B carried 7.06 g of Pd per one liter of the monolithic substrate.

Additionally, 588 g of the powder G, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst B, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst BG (shown in Table 2) at an amount of 60 g per one liter of the monolithic substrate. The catalyst BG carried 3.53 g per one liter of the monolithic substrate. The catalyst BG took a three-layer structure as shown in Fig. 3.

In the column of "HC adsorbing layer" in Table 2, " $\beta(=25)$ " indicates the fact that the HC adsorbing layer contained β -zeolite (having a Si/2Al ratio of 25).

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying system of Example 8 was constructed by disposing the catalyst BG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NOx reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst BG and located at the position of the catalyst 2.

EXAMPLES 9 to 12

[Preparation of Catalyst]

Catalysts CG, DG, EG and FG (shown in Table 2) corresponding respectively to Examples 9, 10, 11 and 12 were obtained repeating the above preparation operation for the catalyst BG with the exception that the powder B was replaced with other powders shown in Table 2, respectively.

[Construction of Exhaust Gas Purifying System]

Each of exhaust gas purifying systems of Examples 9, 10, 11 and 12 (shown in Table 2) was constructed by disposing the catalyst CG, DG, EG or FG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NOx

reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst CG, DG, EG or FG and located at the position of the catalyst 2.

EXAMPLE 13

5 [Preparation of Catalyst]

β -Zeolite ($\text{Si}/2\text{Al} = 25$) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a
10 volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z1 having 100 g of a zeolite coat per one liter of the monolithic substrate.

15 Subsequently, 706 g of the powder B, 706 g of the powder A, 28 g of nitric acid-acidic alumina binder and 1500 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst Z1, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby
20 to obtain a catalyst BA provided with a coat formed on the catalyst Z1 and having a weight of 144 g per one liter of the monolithic substrate. The catalyst BA carried 14.12 g of Pd per one liter of the monolithic substrate.

25 Additionally, 588 g of the powder H, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst BA, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst BAH (shown in Table 2) provided with a coat formed on the
30 catalyst BA and having a weight of 60 g per one liter of the monolithic substrate. The catalyst BAH carried 3.53 g per one liter of the monolithic substrate. The catalyst BAH took a three-layer structure as shown in Fig. 3.

In the column of "First layer" in Table 2, "B+A" indicates the fact that the First layer contained a mixture of the powders B and A.

[Construction of Exhaust Gas Purifying System]

- 5 An exhaust gas purifying systems of Example 13 was constructed by disposing the catalyst BAH in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NOx reducing) catalyst N1 was disposed in the
10 exhaust gas passageway 10a downstream of the catalyst BAH and located at the position of the catalyst 2.

EXAMPLES 14 to 19

[Preparation of Catalyst]

- Catalysts BAI, BAJ, BAK, BAL, BAM and BAN (shown in
15 Table 2) corresponding respectively to Examples 14, 15, 16, 17, 18 and 19 were obtained repeating the above preparation operation for the catalyst BAH with the exception that β -zeolite ($\text{Si}/2\text{Al} = 25$) and the powder H were replaced with other HC adsorbing materials and other powders shown in Table 2, respectively.

- 20 [Construction of Exhaust Gas Purifying System]

- Each of exhaust gas purifying systems of Examples 14, 15, 16, 17, 18 and 19 was constructed by disposing the catalyst BAI, BAJ, BAK, BAL, BAM or BAN in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the
25 position of the catalyst 1, as shown in Fig. 6. Additionally, the (NOx reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst BAI, BAJ, BAK, BAL, BAM or BAN and located at the position of the catalyst 2.

EXAMPLE 20

- 30 [Preparation of Catalyst]

β -Zeolite ($\text{Si}/2\text{Al} = 25$) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a

cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was
5 dried and then fired thereby to obtain a catalyst Z2 having 50 g of a zeolite coat per one liter of the monolithic substrate.

Then, 471 g of the powder O, 9 g of nitric acid-acidic alumina binder and 500 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on an upstream
10 section of the catalyst Z2, so that the walls of the cells were coated with the slurry to form an upstream layer. The upstream section was located upstream relative to flow direction of exhaust gas to be flown through the cells, and had a length of 1/4 of the total length of the monolithic substrate. The catalyst Z2 was dried and fired thereby to
15 obtain a catalyst O1 provided with a coat formed on the catalyst Z2 and having a weight of 48 g per one liter of the monolithic substrate. The catalyst O1 carried 7.06 g of Pd per one liter of the monolithic substrate.

Subsequently, 706 g of the powder B, 706 g of the powder A,
20 28 g of nitric acid-acidic alumina binder and 1000 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on a downstream section of the catalyst O1, so that the walls of the cells were coated with the slurry. The upstream section was located downstream of the upstream section relative to the flow
25 direction of exhaust gas to be flown through the cells, and had a length of 3/4 of the total length of the monolithic substrate. The thus coated catalyst was dried and fired thereby to obtain a catalyst OBA provided with a coat formed on the downstream section of the catalyst O1 and having a weight of 144 g per one liter of the
30 monolithic substrate. The catalyst OBA carried totally 21.18 g of Pd per one liter of the monolithic substrate.

Additionally, 588 g of the powder L, 12g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and

pulverized thereby forming a slurry. The slurry was coated on the downstream side of the catalyst OBA, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst OBAL (shown in Table 2) provided
 5 with a coat formed on the catalyst OBA and having a weight of 60 g per one liter of the monolithic substrate. The catalyst OBAL carried 3.53 g of Rh per one liter of the monolithic substrate. The catalyst OBAL took a structure as shown in Fig. 4.

In the column of "Second layer" in Table 2, "B+A" indicates
 10 the fact that the Second layer contained a mixture of the powder B and the powder A. In the column of "Third layer" in Table 2, "L" indicates the fact that the Third layer contained the powder L.

The HC adsorbing layer, the First layer, the Second layer and the Third layer shown in Table 2 are correspondingly illustrated
 15 in Fig. 4.

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 20 was constructed by disposing the catalyst OBAL in the exhaust gas passageway 10a extending from the internal combustion engine 10
 20 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO_x reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst OBAL and located at the position of the catalyst 2.

EXAMPLES 21 to 25

25 [Preparation of Catalyst]

Catalysts PBBK, QBCJ, RBDI, SBEH and OBFG (shown in Table 2) corresponding respectively to Examples 21, 22, 23, 24 and 25 were obtained repeating the above preparation operation for the catalyst BAH with the exception that β -zeolite ($\text{Si}/2\text{Al} = 25$), the
 30 powder O (in the first layer), the powders B and A (in the second layer) and/or the powder L (in the third layer) were replaced with other HC adsorbing materials and other powders shown in Table 2, respectively.

In the column of "Second layer" in Table 2, "2 x B" indicates the fact that the Second layer contained two the powder B of an amount of two times of that in the catalyst OBAL was contained in the Second layer.

5 [Construction of Exhaust Gas Purifying System]

Each of exhaust gas purifying systems of Examples 21 to 25 was constructed by disposing the catalyst PBBK to OBFG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO_x reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst PBBK to OBFG and located at the position of the catalyst 2.

EXAMPLE 26

[Preparation of Catalyst]

15 β -Zeolite (Si/2Al = 25) in an amount of 900 g was mixed with 100 g of silica sol and 1000 g of pure water, followed by pulverizing, thereby forming a slurry. The slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 4 mil, so that the walls of the cells were coated with the slurry. The thus coated substrate was dried and then fired thereby to obtain a catalyst Z2 having 50 g of a zeolite coat per one liter of the monolithic substrate.

25 Then, 706 g of the powder B and 14g of nitric acid-acidic alumina binder and 1000 g of pure water were mixed and pulverized thereby forming a slurry. The slurry was coated on the catalyst Z2, so that the walls of the cells were coated with the slurry. The thus coated catalyst Z2 was dried and fired thereby to obtain a catalyst B2 provided with a coat formed on the catalyst Z2 and having a weight of 72 g per one liter of the monolithic substrate. The catalyst B2 carried 7.06 g of Pd per one liter of the monolithic substrate.

30 Subsequently, 588 g of the powder G, 12 g of nitric acid-acidic alumina binder and 600 g of pure water were mixed and

pulverized thereby forming a slurry. The slurry was coated on the catalyst B2, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst BG provided with a coat formed on the catalyst B2 and having a weight of 60 g per one liter of the monolithic substrate. The catalyst BG carried 3.53 g of Rh per one liter of the monolithic substrate.

Additionally, 618 g of the powder T, 530 g of the powder U, 88 g of the powder V, 20 g of sodium hydroxide (calculated as Na_2O), 20 g of barium acetate (calculated as BaO), 14 g of nitric acid-acidic alumina binder and 1500 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on the catalyst BG, so that the walls of the cells were coated with the slurry. The thus coated catalyst was dried and fired thereby to obtain a catalyst BGN1 provided with a coat formed on the catalyst BG and having a weight of 147 g per one liter of the monolithic substrate. The catalyst BGN1 carried 12.0 g of Pd, 3.18 g of Pt and 3.88 g of Rh per one liter of the monolithic substrate. The catalyst BGN1 took a structure shown in Fig. 5.

The HC adsorbing layer, the First layer, the Second layer and the Third layer shown in Table 2 are correspondingly illustrated in Fig. 5.

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 26 was constructed by disposing the catalyst BGN1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the (NO_x reducing) catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst BGN1 and located at the position of the catalyst 2.

EXAMPLE 27

[Preparation of NO_x reducing Catalyst]

09256369-052404

A (NOx reducing) catalyst N2 was obtained by repeating the above preparation operation for the catalyst N1 in Example 1 with the exception that sodium hydroxide was replaced with magnesium acetate, in which 10g of MgO and 10 g of BaO were carried per one liter of the monolithic substrate.

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 27 was constructed by disposing the catalyst AG1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst AG1 and located at the position of the catalyst 2.

EXAMPLE 28

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 28 was constructed by disposing the catalyst BGN1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst BA1 and located at the position of the catalyst 2.

EXAMPLE 29

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 29 was constructed by disposing the catalyst BAH in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst BAH and located at the position of the catalyst 2.

EXAMPLE 30

[Construction of Exhaust Gas Purifying System]

An exhaust gas purifying systems of Example 30 was constructed by disposing the catalyst OBFG in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N2 was disposed in the exhaust gas passageway 10a downstream of the catalyst OBFG and located at the position of the catalyst 2.

COMPARATIVE EXAMPLE 1

[Preparation of Three-way catalyst]

10 The powder T in an amount of 565 g, 226 g of the powder F, 10 g of barium acetate (calculated as BaO), 9 g of nitric acid-acidic alumina binder and 1000 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on a cordierite ceramic honeycomb-type monolithic substrate having a
15 volume of 1.3 liters and 900 cells per square inch and having a thickness of walls (defining each cell) of 2 mil, so that the walls of the cells were coated with the slurry. The thus coated monolithic substrate was dried and fired thereby to obtain a catalyst T0 provided with a coat formed on the monolithic substrate and having
20 a weight of 90 g per one liter of the monolithic substrate.

Subsequently, 128 g of the powder V, 200 g of $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ powder, 12 g of nitric acid-acidic alumina binder and 500 g of pure water were mixed, followed by pulverizing, thereby forming a slurry. This slurry was coated on the catalyst T0 so that the walls of the
25 cells were coated with the slurry, followed by drying and firing, thereby to obtain a catalyst T1 provided with a coat formed on the catalyst T0 and having a weight of 34 g per one liter of the monolithic substrate. The catalyst T1 carried 5.65 g of Pd and 0.51 g of Rh per one liter of the monolithic substrate. The catalyst T1 took
30 such a structure in which two layers of coat were formed on the monolithic substrate.

[Construction of Exhaust Gas Purifying System]

09856369-052404

An exhaust gas purifying systems of Comparative Example 1 was constructed by disposing the catalyst T1 in the exhaust gas passageway 10a extending from the internal combustion engine 10 and located at the position of the catalyst 1, as shown in Fig. 6. Additionally, the NOx reducing catalyst N1 was disposed in the exhaust gas passageway 10a downstream of the catalyst T1 and located at the position of the catalyst 2.

EVALUATION OF PERFORMANCE OF EXHAUST GAS PURIFYING CATALYST

Evaluation test (for emission performance) was conducted on the exhaust gas purifying systems of Examples and Comparative Examples, using an evaluation engine system as shown in Fig. 6. For the evaluation test, each exhaust gas purifying system was incorporated in the evaluation engine system including the engine 10 which was a cylinder direct injection internal combustion engine having a displacement of 1.8 liters and produced by Nissan Motor Co., Ltd.

Prior to the evaluation test, the catalysts (corresponding to the catalyst 1 in Fig. 6) of Examples and Comparative Example underwent a durability test in which each catalyst was connected to an internal combustion engine produced by Nissan Motor Co., Ltd. In the durability test, the engine was operated under the following test conditions:

Displacement of the engine: 3,000 cc;

Fuel: "Nisseki Dasshu Gasoline" produced by Nippon Oil Co., Ltd. and having a Pb content of 0 mg/usg (US gallon) and a S content of not more than 30 ppm;

Temperature of gas to be supplied to the catalyst: 650 °C;
and

Time of operation of the engine: 50 hours.

Then, the catalyst 1 undergone the durability test was subjected to the emission performance evaluation test conducted under a test mode "FTP-75 (LA-4) mode" employed in the Unites

States of America. In this test, the exhaust gas purifying system was incorporated in the evaluation engine system of Fig. 6, in the catalyst 1 was installed at its predetermined position shown in Fig. 6. The engine was arranged such that fuel was directly injected into each cylinder. In the emission performance evaluation test, the catalyst 1 and the catalyst 2 had the following volumes:

Catalyst 1: 1.3 liters

Catalyst 2: 1.3 liters

In the emission performance evaluation test, a concentration A of gas components (HC, CO and NOx) in exhaust gas from the engine in a state where no exhaust gas purifying system was provided was measured, and a concentration B in exhaust gas emitted from the catalyst 2 (NOx reducing catalyst) in Fig. 6 was measured, thereby obtaining a "remaining rate (%)" of the gas components, shown in Table 3. The remaining rate (%) was calculated by [(the concentration B of the gas component / the concentration A of the gas component) x 100], in which the concentrations were measured as "ppm"

As apparent from the above, according to the present invention, by virtue of the catalytic layer for functioning to produce hydrogen (H₂), the produced hydrogen is used as reducing agent. As a result, the catalyst of the present invention can reduce and remove NOx in exhaust gas at a high efficiency under the oxygen-excessive atmosphere of exhaust gas and effectively removing HC and CO particularly during a low temperature engine operation immediately after engine starting, while obtaining a high fuel economy improvement effect upon making lean-burn operation of the engine.

The entire contents of Japanese Patent Applications P11-336839 (filed November 26, 1999) and P2000-342550 (filed November 9, 2000) are incorporated herein by reference.

Although the invention has been described above by reference to certain embodiments of the invention, the invention is not limited to the embodiments and examples described above.

Modifications and variations of the embodiments and examples described above will occur to those skilled in the art, in light of the above teachings. The scope of the invention is defined with reference to the following claims.

5 INDUSTRIAL APPLICABILITY

As discussed above, the exhaust gas purifying catalyst according to the present invention can be applied to reduce and remove NO_x in exhaust gas at a high efficiency under the oxygen-excessive atmosphere of exhaust gas and effectively removing HC and CO, maintaining a high fuel economy improvement effect under lean-burn operation.

10

TABLE 1

Powder (catalyst component)	Metal carried		Carrier
	Kind	Concentration (%)	
A	Pd	10.0	CeO ₂
B	Pd	10.0	Zr _{0.1} Ce _{0.9} O ₂
C	Pd	10.0	Zr _{0.2} Ce _{0.8} O ₂
D	Pd	10.0	Zr _{0.5} Ce _{0.5} O ₂
E	Pd	10.0	Zr _{0.9} Ce _{0.1} O ₂
F	Pd	5.0	CeO ₂
G	Rh	6.0	Ca _{0.2} Zr _{0.8} O ₂
H	Rh	6.0	Mg _{0.1} Zr _{0.9} O ₂
I	Rh	6.0	Ba _{0.1} Zr _{0.9} O ₂
J	Rh	6.0	Sr _{0.2} Zr _{0.8} O ₂
K	Rh	6.0	Ca _{0.1} Mg _{0.1} Zr _{0.8} O ₂
L	Rh	6.0	Ca _{0.1} Ba _{0.05} Mg _{0.05} Zr _{0.8} O ₂
M	Rh	6.0	Ca _{0.01} Zr _{0.99} O ₂
N	Rh	6.0	Ca _{0.5} Zr _{0.5} O ₂
O	Pd	15.0	Al ₂ O ₃
P	Pd	15.0	Ce(3wt.%) - Al ₂ O ₃
Q	Pd	15.0	Zr(3wt.%) - Al ₂ O ₃
R	Pd	15.0	La(3wt.%) - Al ₂ O ₃
S	Pd	15.0	Zr(10wt.%) - Al ₂ O ₃
T	Pd	8.0	Al ₂ O ₃
U	Pt	6.0	Al ₂ O ₃
V	Rh	4.0	Al ₂ O ₃

TABLE 2

Catalyst	Structure of catalyst	Substance carried				HC adsorbing layer	First layer	Second layer	Third layer
		Pd	Pt	Rh	Alkali metal oxide	Alkaline earth metal oxide			
AG1	Fig.3	7.06	-	3.53	-	-	A	G	-
AG2	Fig.3	7.06	-	3.53	-	-	A	G	-
AG3	Fig.3	7.06	-	3.53	-	-	A	G	-
AG4	Fig.3	7.06	-	3.53	-	-	A	G	-
AG5	Fig.3	7.06	-	3.53	-	-	A	G	-
AG6	Fig.3	7.06	-	3.53	-	-	A	G	-
AG7	Fig.3	7.06	-	3.53	-	-	A	G	-
BG	Fig.3	7.06	-	3.53	-	-	B	G	-
CG	Fig.3	7.06	-	3.53	-	-	C	G	-
DG	Fig.3	7.06	-	3.53	-	-	D	G	-
EG	Fig.3	7.06	-	3.53	-	-	E	G	-
FG	Fig.3	7.06	-	3.53	-	-	F	G	-
BAH	Fig.3	14.12	-	3.53	-	-	B+A	H	-
BAI	Fig.3	14.12	-	3.53	-	-	B+A	I	-
BAJ	Fig.3	14.12	-	3.53	-	-	B+A	J	-
BAK	Fig.3	14.12	-	3.53	-	-	B+A	K	-
BAL	Fig.3	14.12	-	3.53	-	-	B+A	L	-
BAM	Fig.3	14.12	-	3.53	-	-	B+A	M	-
BAN	Fig.3	14.12	-	3.53	-	-	B+A	N	-
OBAL	Fig.4	21.18	-	3.53	-	-	O	B+A	L
PBBK	Fig.4	21.18	-	3.53	-	-	P	2×B	K
QBCJ	Fig.4	21.18	-	3.53	-	-	Q	B+C	J
RBDI	Fig.4	21.18	-	3.53	-	-	R	B+D	I
SBEH	Fig.4	21.18	-	3.53	-	-	S	B+E	H
OBFG	Fig.4	21.18	-	3.53	-	-	O	B+F	G
BGN1	Fig.5	12.0	3.18	3.88	(Na ₂ O) ₂	(BaO) ₂₀	B	G	T+U+V
N1	Single layer	4.94	3.18	0.35	(Na ₂ O) ₂	(BaO) ₂₀			
N2	Single layer	4.94	3.18	0.35	(MgO) ₁₀	(BaO) ₁₀			
T1	Two layers	5.65	-	0.51	-	(BaO) ₁₀			

TABLE 3

	Installation position		Remaining rate (%)		
	Catalyst 1	Catalyst 2	HC	CO	NOx
Example 1	AG1	N1	1.3	1.9	2.4
Example 2	AG2	N1	1.2	1.8	2.2
Example 3	AG3	N1	1.1	1.7	2.1
Example 4	AG4	N1	1.1	1.8	1.9
Example 5	AG5	N1	1.2	1.8	2.0
Example 6	AG6	N1	1.2	1.7	2.0
Example 7	AG7	N1	1.2	1.8	2.1
Example 8	BG	N1	1.2	1.7	1.9
Example 9	CG	N1	1.3	1.6	2.1
Example 10	DG	N1	1.3	1.6	2.2
Example 11	EG	N1	1.2	1.7	2.0
Example 12	FG	N1	1.2	1.8	2.1
Example 13	BAH	N1	1.1	1.9	1.9
Example 14	BAI	N1	1.1	1.8	1.9
Example 15	BAJ	N1	1.1	1.8	2.0
Example 16	BAK	N1	1.2	1.8	2.0
Example 17	BAL	N1	1.1	1.9	2.1
Example 18	BAM	N1	1.2	1.8	2.1
Example 19	BAN	N1	1.3	1.8	2.2
Example 20	OBAL	N1	1.4	2.0	2.2
Example 21	PBBK	N1	1.2	1.8	2.1
Example 22	QBCJ	N1	1.1	1.9	1.9
Example 23	RBDI	N1	1.1	1.8	1.9
Example 24	SBEH	N1	1.1	1.8	2.0
Example 25	OBFG	N1	1.2	1.8	2.0
Example 26	BGN1	N1	1.3	2.4	2.2
Example 27	AG1	N2	1.2	1.7	2.0
Example 28	BG1	N2	1.3	1.6	2.1
Example 29	BAH	N2	1.2	1.7	2.1
Example 30	OBFG	N2	1.1	1.8	2.0
Comp. example 1	TI	N1	4.2	7.1	7.3

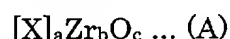
CLAIMS

1. An exhaust gas purifying catalyst comprising:
a monolithic substrate;
a HC adsorbing layer for adsorbing hydrocarbons (HC),
5 said HC adsorbing layer containing zeolite and being formed on said monolithic substrate;
a catalytic layer for producing hydrogen (H₂) and reducing NO_x, said catalytic layer functioning to produce hydrogen (H₂) from at least one of hydrocarbons and carbon monoxide (CO) and to
10 reduce nitrogen oxides (NO_x) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas, said catalytic layer being formed on said HC adsorbing layer.
2. An exhaust gas purifying catalyst as claimed in Claim 1,
15 wherein said exhaust gas purifying catalyst is for purifying exhaust gas discharged from an internal combustion engine, wherein said HC adsorbing layer contains zeolite and functions to adsorb hydrocarbons during a cold operation of the engine and to release adsorbed hydrocarbons during a warm-up operation of the engine,
20 wherein said catalytic layer functions to produce hydrogen from hydrocarbons released from said HC adsorbing layer and from at least one of hydrocarbons and carbon monoxide discharged from the engine after the warm-up operation and to reduce NO_x with produced hydrogen and at least hydrocarbons and carbon monoxide
25 in exhaust gas.
3. An exhaust gas purifying catalyst as claimed in Claim 1 or 2, wherein said catalytic layer contains a H₂ producing catalyst component for functioning to produce hydrocarbons, and a NO_x
30 reducing catalyst component for functioning to reduce nitrogen oxides, said H₂ producing catalyst component being disposed on said HC adsorbing layer and including a HC reforming catalyst component functioning to reform hydrocarbons so as to produce

hydrogen and a CO reforming catalyst component functioning to make steam reforming of carbon monoxide, said HC reforming catalyst component containing cerium oxide carrying palladium, said CO reforming catalyst component containing zirconium oxide carrying rhodium.

4. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 3, wherein said catalytic layer further includes an upstream layer formed at an upstream section of said exhaust gas purifying catalyst, said upstream section being located upstream of said HC reforming catalyst component layer and said CO reforming catalyst component layer relative to flow direction of exhaust gas, said upstream layer containing alumina carrying palladium.

5. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 4, wherein said zirconium oxide carrying rhodium contains alkaline earth and has a composition represented by the following formula (A):



where X is an alkaline earth metal selected from the group consisting of magnesium, calcium, strontium and barium; a and b are ratios of atoms of elements; and c is a number of oxygen atoms required for satisfying valences of X and Zr, in which a is within a range of from 0.01 to 0.5, b is within a range of from 0.5 to 0.99, and $a+b = 1.0$.

6. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 5, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium.

7. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 6, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NOx reducing catalyst component containing at least one selected from the group consisting of palladium, platinum, rhodium, alumina, alkali metal and alkaline earth metal.
8. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 7, wherein said zeolite contains H-type β -zeolite having a Si/2Al ratio ranging from 10 to 500.
9. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 8, wherein said zeolite contains H-type β -zeolite and at least one of MFI, Y-type zeolite, USY-type zeolite and mordenite.
10. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 9, wherein said zeolite contains at least one selected from the group consisting of palladium, magnesium, calcium, strontium, barium, silver, yttrium, lanthanum, cerium, neodymium, phosphorus, boron and zirconium.
11. An exhaust gas purifying catalyst as claimed in any of Claims 1 to 10, wherein a NOx reducing catalyst component functioning to reduce nitrogen oxides is contained in at least one of said HC adsorbing layer, said HC reforming layer, said CO reforming layer and said upstream layer containing alumina carrying palladium, said NOx reducing catalyst component containing at least one selected from the group consisting of alkali metal and alkaline earth metal, said NOx reducing catalyst

component containing at least one selected from the group consisting of potassium, cesium, magnesium, calcium and barium.

12. An exhaust gas purifying catalyst as claimed in Claim 3,
5 wherein said HC reforming catalyst component and said CO reforming catalyst are mixed to form a single layer disposed on said monolithic substrate on said HC adsorbing layer.

13. An exhaust gas purifying catalyst as claimed in Claim 3,
10 wherein said HC reforming catalyst component forms a first layer disposed on said monolithic substrate, and said CO reforming catalyst forms a second layer, said second layer being formed on said first layer.

14. An exhaust gas purifying catalyst as claimed in Claim 3,
15 wherein said HC reforming catalyst component forms a first layer disposed on said monolithic substrate, and said CO reforming catalyst component forms a second layer, said second layer being formed downstream of said first layer relative to flow direction of
20 exhaust gas.

15. An exhaust gas purifying system for an internal combustion engine, comprising:

an exhaust gas purifying catalyst including

25 a monolithic substrate,
a HC adsorbing layer for adsorbing hydrocarbons (HC), said HC absorbing layer being formed on said monolithic substrate, and

30 a catalytic layer for producing hydrogen (H₂) and reducing NO_x, said catalytic layer functioning to produce hydrogen (H₂) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO_x) with the produced hydrogen and

at least one of hydrocarbons and carbon monoxide in exhaust gas, said catalytic layer being formed on said HC adsorbing layer; and

- 5 a device for controlling combustion in the engine to produce exhaust gas, to be brought into contact with said catalytic layer, having a composition meeting a relation [(a concentration of hydrogen / a concentration of total reducing components) \geq 0.3].

16. A method of producing an exhaust gas purifying catalyst, comprising:

- 10 preparing a monolithic substrate;
forming a HC adsorbing layer on said monolithic layer, to adsorb hydrocarbons (HC); and
forming a catalytic layer on said HC adsorbing layer, to produce hydrogen (H₂) and reduce NO_x, said catalytic layer
15 functioning to produce hydrogen (H₂) from at least one of hydrocarbons and carbon monoxide (CO) and to reduce nitrogen oxides (NO_x) with the produced hydrogen and at least one of hydrocarbons and carbon monoxide in exhaust gas.

FIG.2

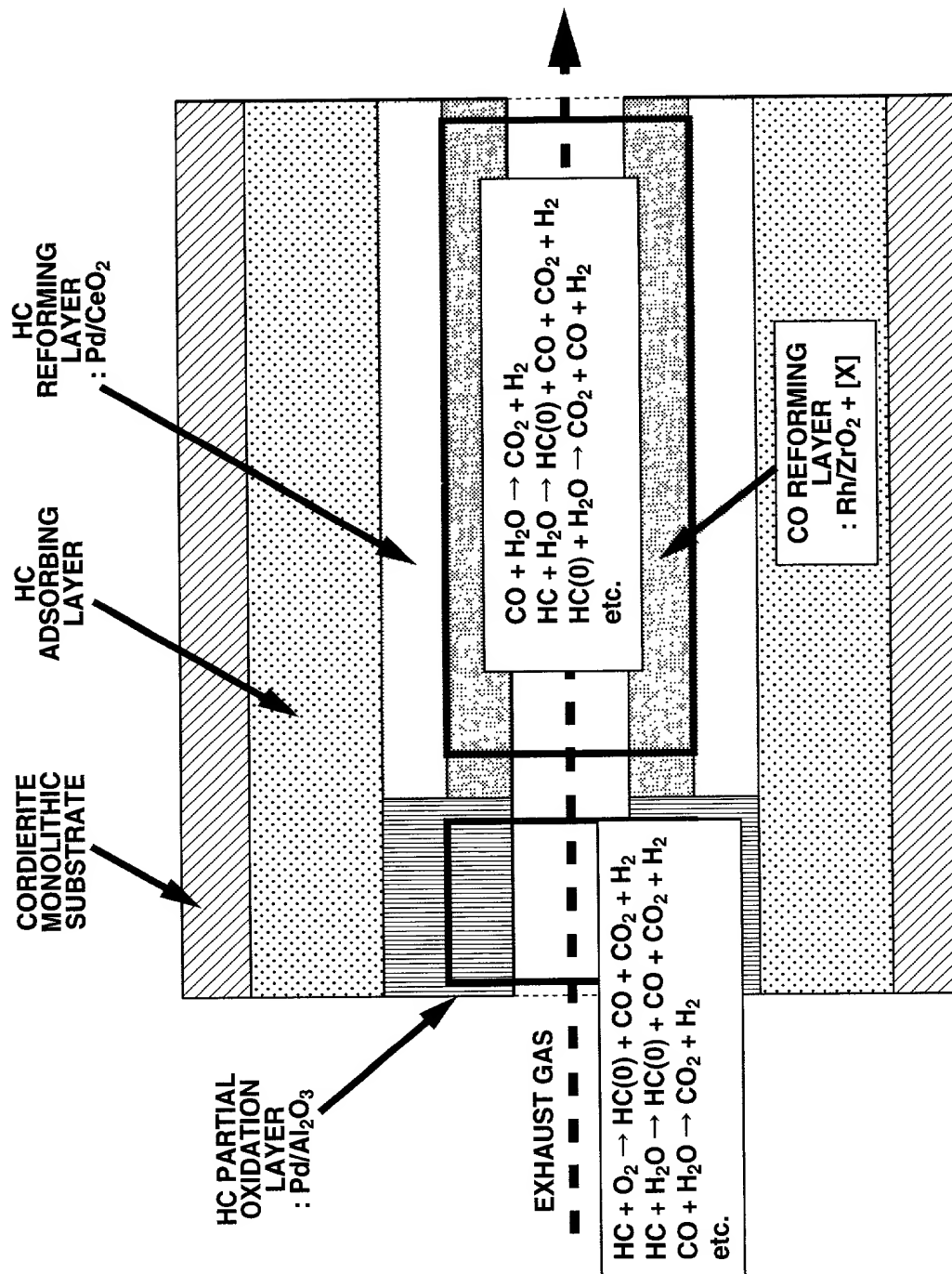


FIG.3

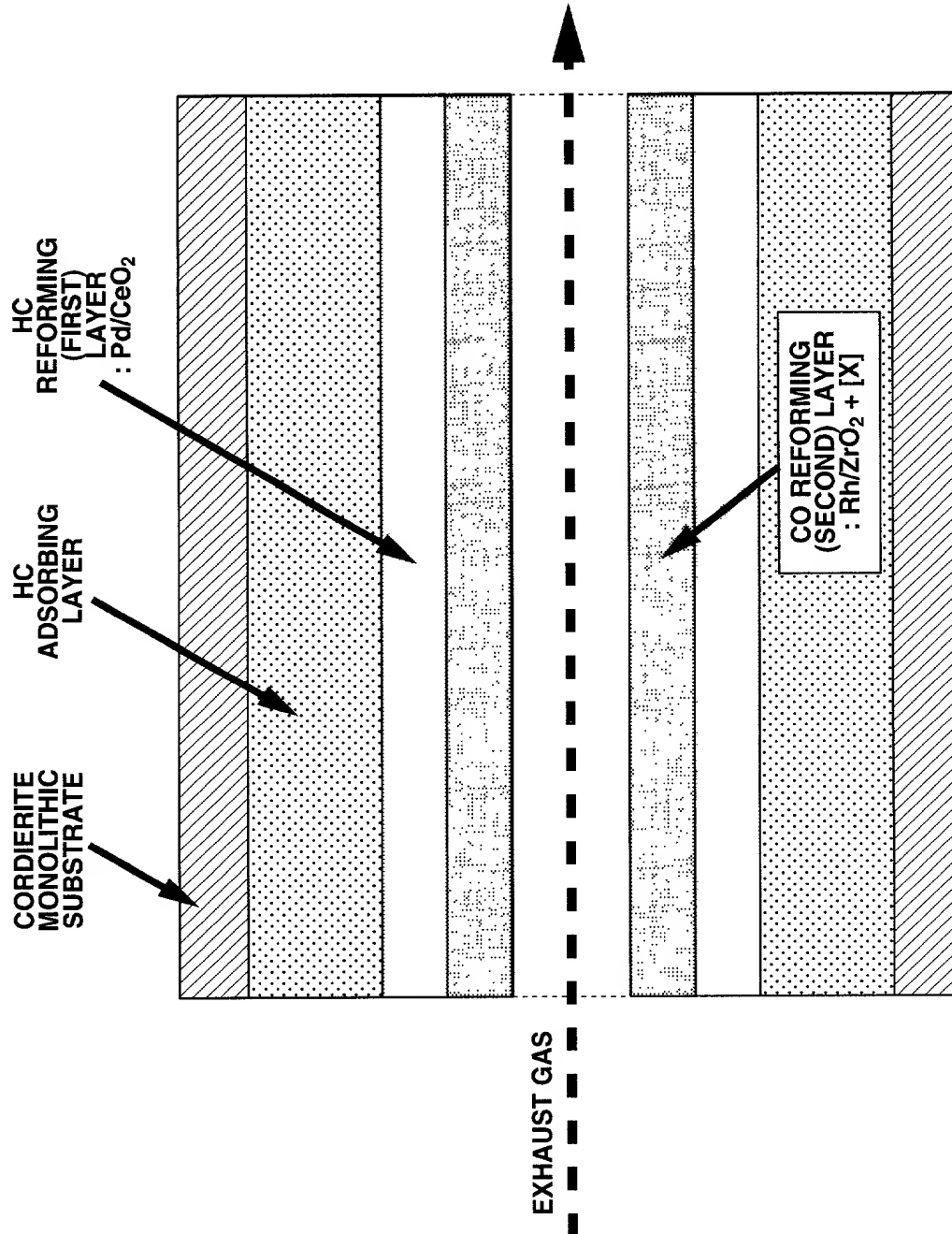


FIG.4

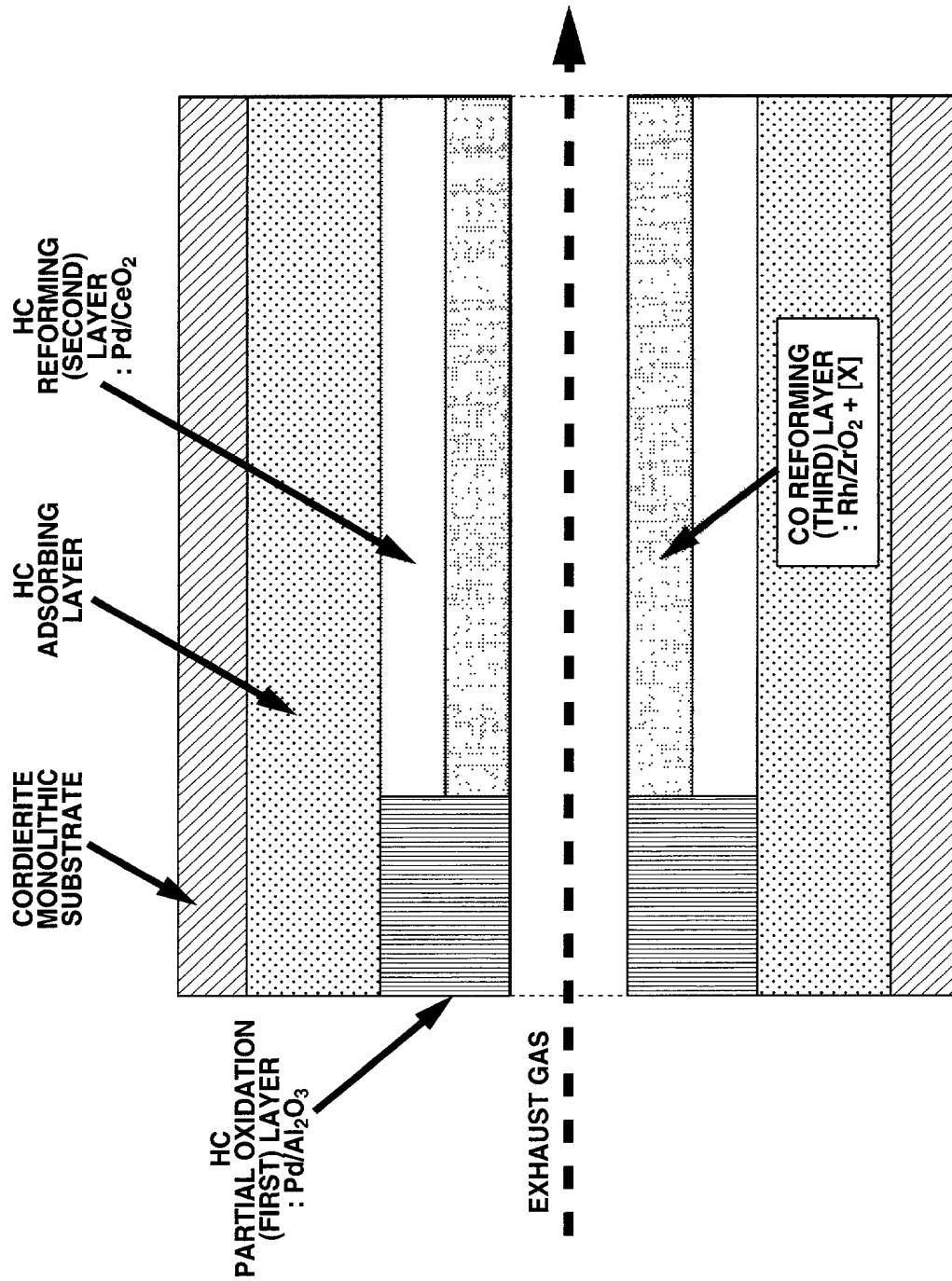


FIG.5

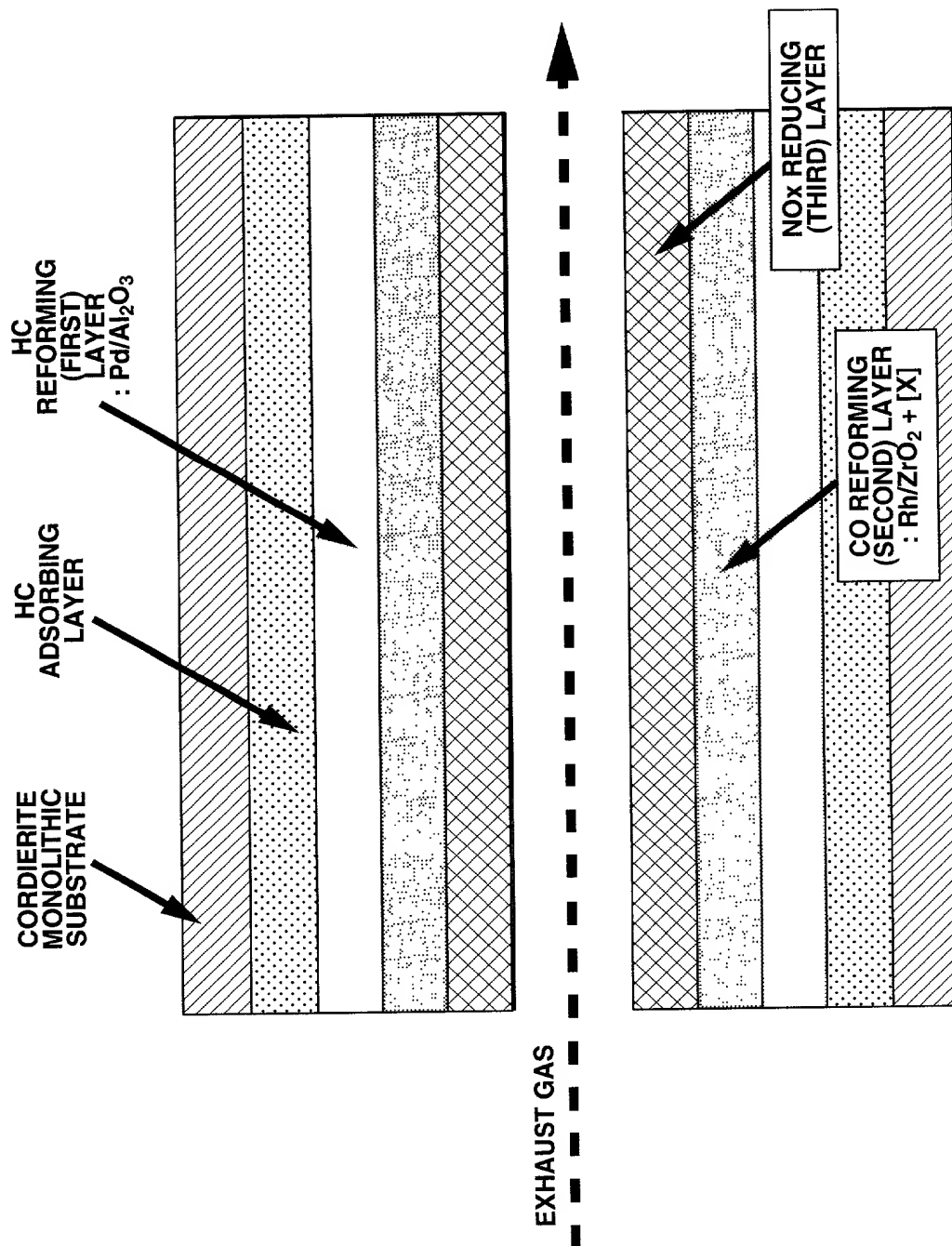
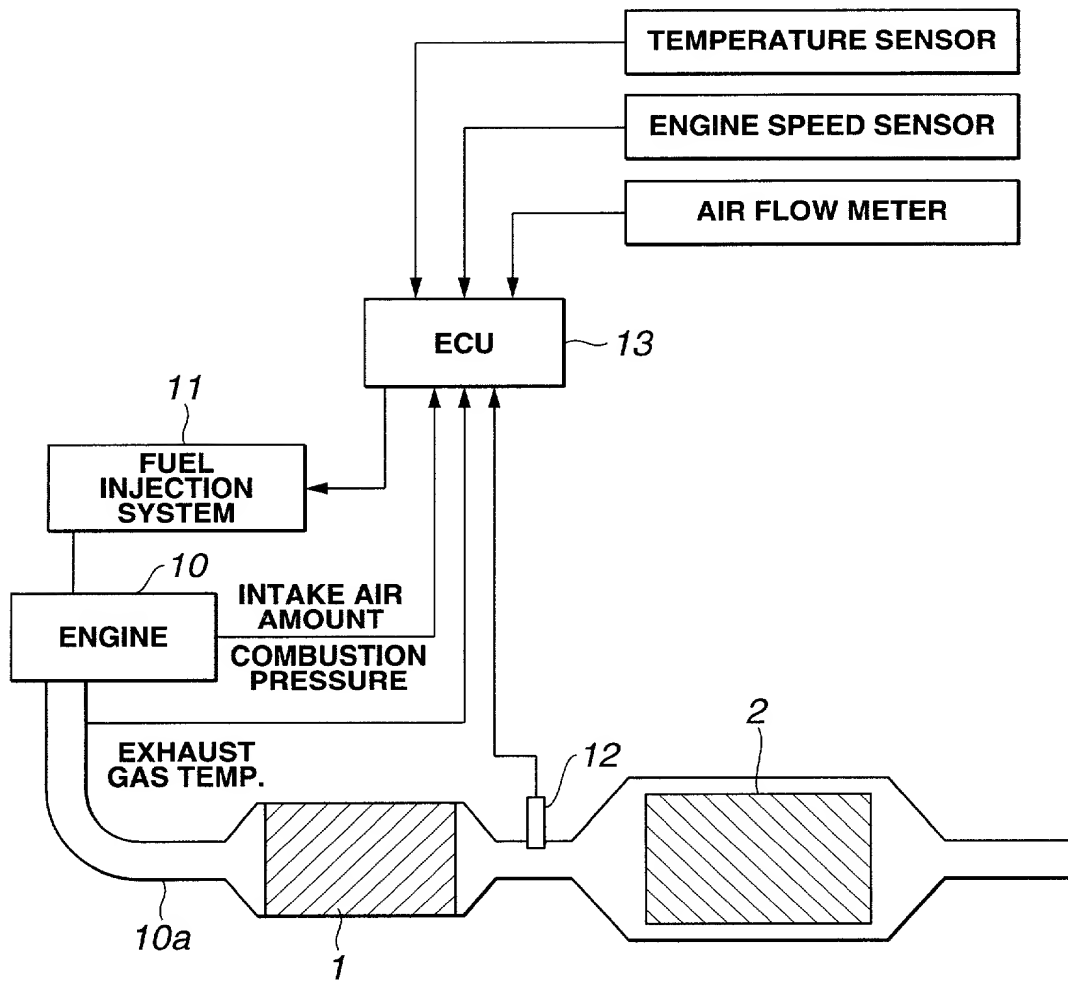


FIG.6



DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I HEREBY DECLARE:

THAT my residence, post office address, and citizenship are as stated below next to my name;

THAT I believe I am the original, first, and sole inventor (if only one inventor is named below) or an original, first, and joint inventor (if plural inventors are named below or in an attached Declaration) of the subject matter which is claimed and for which a patent is sought on the invention entitled

EXHAUST GAS PURIFYING CATALYST

the specification of which (check one)

_____ is attached hereto.

X was filed on November 21, 2000 as United States Application Number or PCT International Application Number PCT/JP00/08180 and was amended on _____ (if applicable).

THAT I do not know and do not believe that the same invention was ever known or used by others in the United States of America, or was patented or described in any printed publication in any country, before I (we) invented it;

THAT I do not know and do not believe that the same invention was patented or described in any printed publication in any country, or in public use or on sale in the United States of America, for more than one year prior to the filing date of this United States application;

THAT I do not know and do not believe that the same invention was first patented or made the subject of an inventor's certificate that issued in any country foreign to the United States of America before the filing date of this United States application if the foreign application was filed by me (us), or by my (our) legal representatives or assigns, more than twelve months (six months for design patents) prior to the filing date of this United States application;

THAT I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment specifically referred to above;

THAT I believe that the above-identified specification contains a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the invention, and sets forth the best mode contemplated by me of carrying out the invention; and

THAT I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

0955360-092101

I HEREBY CLAIM foreign priority benefits under Title 35, United States Code § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number	Country	Foreign Filing Date	Priority Claimed?	Certified Copy Attached?
11-336839	Japan	26 November 1999	Yes	
2000-342550	Japan	9 November 2000	Yes	
PCT/JP00/08180	Japan	21 November 2000	Yes	

I HEREBY CLAIM the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

U.S. Provisional Application Number	Filing Date

I HEREBY CLAIM the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Application Number	Parent Filing Date	Parent Patent Number

I HEREBY APPOINT the following registered attorneys and agents of the law firm of FOLEY & LARDNER to have full power to prosecute this application and any continuations, divisions, reissues, and reexaminations thereof, to receive the patent, and to transact all business in the United States Patent and Trademark Office connected therewith:

STEPHEN A. BENT
 DAVID A. BLUMENTHAL
 ALAN I. CANTOR
 WILLIAM T. ELLIS
 JOHN J. FELDHAUS
 PATRICIA D. GRANADOS
 JOHN P. ISACSON

Reg. No. 29,768
 Reg. No. ~~26,257~~
 Reg. No. ~~28,163~~
 Reg. No. ~~26,874~~
 Reg. No. ~~28,822~~
 Reg. No. ~~33,683~~
 Reg. No. 33,715

MICHAEL D. KAMINSKI	Reg. No. <u>32,904</u>
LYLE KIMMS	Reg. No. <u>34,079</u>
KENNETH E. KROSIN	Reg. No. <u>25,735</u>
JOHNNY A. KUMAR	Reg. No. <u>34,649</u>
GLENN LAW	Reg. No. <u>34,371</u>
PETER G. MACK	Reg. No. <u>26,001</u>
BRIAN J. MC NAMARA	Reg. No. <u>32,789</u>
SYBIL MELOY	Reg. No. <u>22,749</u>
RICHARD C. PEET	Reg. No. <u>35,792</u>
GEORGE E. QUILLIN	Reg. No. <u>32,792</u>
COLIN G. SANDERCOCK	Reg. No. <u>31,298</u>
BERNHARD D. SAXE	Reg. No. <u>28,665</u>
CHARLES F. SCHILL	Reg. No. <u>27,590</u>
RICHARD L. SCHWAAB	Reg. No. <u>25,479</u>
ARTHUR SCHWARTZ	Reg. No. <u>22,115</u>
HAROLD C. WEGNER	Reg. No. <u>25,258</u>

and I request that all correspondence be directed to:

~~Richard L. Schwaab~~
~~FOLEY & LARDNER~~
~~Washington Harbour~~
~~3000 K Street, N.W., Suite 500~~
~~P.O. Box 25696~~
~~Washington, D.C. 20007-8696~~

Telephone: (202) 672-5300
 Facsimile: (202) 672-5399

I UNDERSTAND AND AGREE THAT the foregoing attorneys and agents appointed by me to prosecute this application do not personally represent me or my legal interests, but instead represent the interests of the legal owner(s) of the invention described in this application.

I FURTHER DECLARE THAT all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Name of first inventor	<u>Shinji YAMAMOTO</u>
Residence	<u>Kanagawa, Japan</u> <i>JK</i>
Citizenship	<u>Japanese</u>
Post Office Address	<u>1-44-15, Koyabe, Yokosuka-shi, Kanagawa</u>
	<u>238-0026 Japan</u>
Inventor's signature	<u><i>Shinji Yamamoto</i></u>
Date	<u>5/8/2001</u>